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Leaching of Radioactive Isotopes from Waste Solids

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The most commonly used empirical model for the quantity Q of a radioactive isotope leached from a solidified waste as a function of time t is $Q=at^{1/2}+bt$, where a and b are empirically determined constants for a specific leach process involving a specific isotope. This formula works well for many solid wastes and can be derived theoretically from a model employing Fickian diffusion. However, the formula is known to be totally inaccurate for my other solids and also in particular for glassy solids which devitrify. Since devitrification and other symptoms of aging are commonly occurring processes in the long term storage of radioactive waste, it is important to have a correct alternative formula for Q and even more important to understand the physical processes involved in leaching.

A theoretical model involving a generalized, non-Fickian mechanism for diffusion is derived in this paper and applied to determine Q as a function of time t. It is found, on the basis of this type of diffusion which occurs in devitrified glassy solids and other solid waste materials that $Q=At^{1/4}+Bt^{3/4}$. Here A and B are constants which can be determined empirically, and they can also be determined phenomenologically in terms of the fundamental parameters of the diffusion model. When both formulas are normalized to a common value, at some instant the new formula predicts larger initial quantities and faster initial leach rates.

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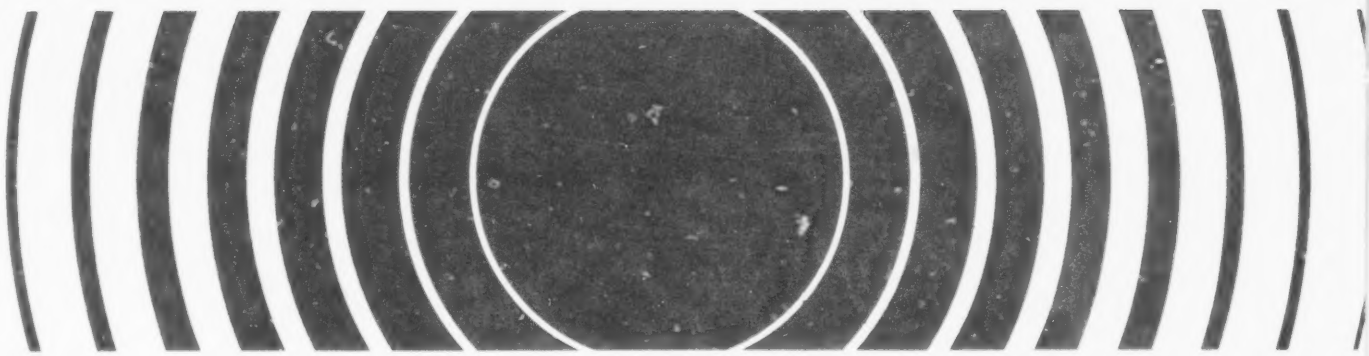

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Abstract

The most commonly used empirical model for the quantity Q of a radioactive isotope leached from a solidified waste as a function of time t is $Q = at^{1/2} + bt$, where a and b are empirically determined constants for a specific leach process involving a specific isotope. This formula works well for many solid wastes and can be derived theoretically from a model employing Fickian diffusion. However, the formula is known to be totally inaccurate for many other solids and also in particular for glassy solids which devitrify. Since devitrification and other symptoms of aging are commonly-occurring processes in the long term storage of radioactive waste, it is important to have a correct alternative formula for Q and even more important to understand the physical processes involved in leaching.

A theoretical model involving a generalized, non-Fickian mechanism for diffusion is derived in this paper and applied to determine Q as a function of time t. It is found, on the basis of this type of diffusion which occurs in devitrified glassy solids and other solid waste materials, that $Q=At^{1/4} + Bt^{3/4}$. Here A and B are constants which can be determined empirically, and they can also be determined phenomenologically in terms of the fundamental parameters of the diffusion model. When both formulas are normalized to a common value, at some instant the new formula predicts larger initial quantities and faster initial leach rates.

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1. Introduction

It is essential for safety, engineering, and economic considerations that we have reliable estimates of the amount of radioactivity that enters the environment as a result of the treatment, storage, transport, and disposal of radioactive waste. We shall consider the effects of leaching on solidified radioactive waste materials. Leaching of a waste deposit by groundwater followed by transport in an aqueous solution is a commonly occurring situation. The leach resistance of solidified waste materials in groundwater is often cited as the critical factor for the decision to use such methods of disposal for the long term isolation of high level radioactive waste [1]-[3]. In particular, because of its assumed high resistance to leaching, glass (and various other forms of vitreous, ceramic, and plastic materials) are currently popular for storing high level wastes [3]. The storage periods of interest range from tens of years to periods of approximately 100,000 years.

The most important information sought is a reliable estimate of the quantity Q of a radioactive isotope leached from a solidified waste as a function of time t, and the most commonly used empirical model for Q is

$$Q = at^{\frac{1}{2}} + bt. \tag{1.1}$$

Here a and b are empirically determined constants for a specific leach process involving a specific isotope. There are some other competing expressions [1] for Q which attempt to account for on-site factors which would not occur in standard laboratory tests. The formula (1.1) was developed from studies on the leaching of commercial glasses by aqueous solutions [2], [4]-[7], and it seems to be very accurate for many glasses as long as the glass matrix does not devitrify [2], [4]. When devitrification occurs (as in certain

phosphate-glass products, for example,[2], [8]), the leachability is increased by a factor of approximately one thousand. Apparently, no expression (empirical or theoretical) is given in any of the open literature for the quantity Q of this type of material which is leached. Godbee and Joy [2] state that their mechanisms can not account for these situations and recommend further studies exploring alternative combinations of fundamental mechanisms to account for and predict the leach behavior of these materials. We present one possible explanation here together with a time law to replace (1.1).

Normally,in such a critical situation as the storage and disposal of high level radioactive waste,it would obviously be prudent to recommend as containers vitreous solids which are known to be highly resistant to devitrification under the circumstances assumed to be encountered. Recently reported experimental results [3], [9], however, show that the radioactive isotopes embedded in a vitreous solid can interact in subtle ways with the glass to enhance the "aging" (i.e., devitrification, increased porosity, phase separation, etc.) of a vitreous container made from glasses previously thought particularly stable to leaching. Thus, in addition to further experimental studies on the nature of these phenomena it is desirable to have a reliable formula to replace (1.1) for describing the amount of radioactive isotope leached from a solid in circumstances where (1.1) does not apply (for example, in a devitirfied state, or a state of increased porosity due to increased chemical activity as a result of the embedded radioactive isotope [9]). If leaching and leach rates are dramatically increased in these situations, then several possibilities are suggested: (i) don't use these materials, (ii) attempt to develop ways to "treat" these materials to resist these "aging" processes, or (iii) accept the aging and increased leach amounts but perhaps embed smaller amounts per given amount of container.

In any event reliable estimates of the amount Q of a radioactive isotope leached from a solidified waste as a function of time t are needed. These estimates and formulas are usually derived by empirical means although there are a few theoretical studies [2], [7]. Laboratory experiments to simulate actual (or what are thought to be actual) conditions have been performed (see [2] and the references there) in ways thought to correspond to storage times equivalent to a given number of years. Empirical relations are deduced and extrapolated to longer times and other situations assuming that the system maintains the same physical mechanisms and time dependencies. In addition to experimental studies, theoretical studies should be made with attempts to model the system using fundamental mass transport processes. Such studies have several obvious advantages. For example, the basic physical processes involved will become better understood, empirical constants can be interpreted in terms of the basic parameters of the system, and extrapolation of time laws can be performed with a greater degree of confidence. Godbee and Joy [2] have carried out an excellent theoretical study which substantiates formula (1.1) in many pertinent cases, and they carefully point out situations in which (1.1) does not apply and for which their theory is not applicable. For example, they cite phosphate ceramic products (which readily devitrify) and for which highly elevated leaching amounts are observed as being unexplained according to their theory. For these and other solids we present a theory based on the pioneering work of J.W. Cahn [10]-[12] on various glasses and metal alloys to derive an alternative to (1.1)

2. Generalized diffusion model

Many phenomena influence leach resistance, and the general problem of mass transport through waste solids is very complicated. For example, among the pertinent factors are porosity and fractures in the solid, temperature, chemical composition and reactivity of the storage matrix and its stability when subjected to surrounding conditions and irradiation by the contained radioactive isotopes, solubility of the isotope being leached, characteristics of the leaching solution, possible transport paths which include the inside of crystal lattices, along crystal grain boundaries, etc. When mass transport is known to occur via several mechanisms, most theoretical studies invoke an effective diffusion coefficient and Fickian diffusion. This is the method used in the theoretical studies cited in the Introduction.

The use of an effective diffusion coefficient is an entirely acceptable way to lump many detailed and complicated physical effects into one phenomenological constant which can be experimentally measured. Even if we allow space, time, and concentration-dependent diffusion coefficients, we can still experimentally determine the dependence of the diffusion coefficient on these variables phenomenologically. More fundamental, however, is the assumption of Fickian diffusion. We now show that a more generalized diffusive mechanism is likely to be operating, and we analyze the equations resulting from this assumption.

It is known [5], [10], [13], [14] that many glassy polymers and certain metal alloys exhibit non-Fickian diffusion. Chapter 11 of Crank's book [14] and the excellent survey and expository paper of Cahn [10] describe many experimental observations and various attempts to theoretically and mathematically model these non-Fickian situations. The models of Cahn [10]-[12] seem the most promising, and indeed, they incorporate most of the other models as special cases. Before presenting the derivation appropriate for the present problem

of leaching from waste solids, it may be helpful to briefly recall some of major periods and attempts to generalize Fick's law.

In various fields of physics, chemistry, and engineering in the last one hundred years Fick's law of diffusion has been inadequate to describe diffusive processes. In many cases generalizations and alternatives, based on fundamental physical processes, have been proposed which successfully describe and predict the experimental observations. Three main periods and problems have provided the major impetus for this development. (i) The work of Gibbs and van der Waals around the turn of the century on coexistence near the critical point led to the concepts of nucleation, metastability, and spinodal decomposition in an attempt to understand the simultaneous existence of two spatially distributed states of matter (i.e., pattern formation). The fundamental role of diffusion and its physical nature was carefully studied. (ii) The work of Cahn and his co-workers in the period 1950-1970 on the structure of metal alloys (again, pattern formation) led to a successful analytical formulation incorporating the concepts of a negative diffusion gradient which has been experimentally observed by x-ray techniques and which is necessary in the theory of metal alloys to account for molecular clumping (or aggregation). (iii) The recent work (1970-1980) on striations or patterns (in the phonon or quasi-particle density) on super-conducting thin films led to a re-examination and further development of the Gibbs-van der Waals theories this time based on the pioneering work of Landau. At about the same time as the work on metal alloys was going on, the Landau-Ginzburg theory of non-equilibrium thermodynamics was proposed to account for the phase co-existence patterns. Inherent in this theory is a non-Fickian mechanism of diffusion. The recent work in superconductivity has led to a satisfying theory based on the Landau-Ginzburg description. Excellent papers describing the work on metal alloys and the

earlier phase co-existence problems are the major survey paper of Cahn [10] and his paper [12]. The more recent work in super-conductivity can be found in [15],[16].

The present problem of leaching from waste solids is different from those just mentioned. However, it is just another application of the generalized diffusion model. As Cahn [10] points out, the generalized diffusion model can and has been verified as an appropriate modification of the classical Fickian diffusion equation, and he further states that his particular problem is but one application and that the model should be used in all kinds of diffusion problems. In particular, quite detailed verification [10] of the validity of the generalized model has been carried out for certain metal alloys and various glasses (silica glasses).

We now derive the generalized diffusion equation with a brief plausibility arqument. A more detailed derivation is given in Appendix A. Recall that Fick's law states that the diffusive flux $\underline{J}$ (or equivalently the the mass current $\underline{J}$) is proportional to the concentration gradient; that is,

$$\underline{J} = -D \text{ grad } C, \tag{2.1}$$

where C is the concentration of the diffusing species, and the proportionality constant D is known as the diffusivity (or diffusion coefficient). In general, D can depend on space, time, and even concentration, that is $D = D(\underline{x},t,C)$. The basic equation of continuity (i.e., conservation of mass) then becomes

$$\frac{\partial C}{\partial t} = - \text{ div } \underline{J} = \text{div } (D \text{ grad } C), \tag{2.2}$$

which is the familiar heat or diffusion equation.

Alternatively, following Cahn [10] we can derive (2.2) phenomenologically from a basic thermodynamic or internal energy argument (see Appendix A) by defining a chemical potential μ, the gradient of which drives the mass current $\underline{J}$. That is,

$$\underline{J} = - \text{grad}\, \mu \tag{2.2}$$

If the potential is a function of only the state variable C, then $\mu = \mu(C)$, and

$$\underline{J} = - \text{grad}\, \mu(C) = - \mu'(C)\, \text{grad}\, C. \tag{2.4}$$

The equation of continuity then becomes

$$\frac{\partial C}{\partial t} = - \text{div}\, \underline{J} = \text{div}\, (\mu'(c)\, \text{grad}\, C)\ , \tag{2.5}$$

which is identical with (2.2) if we make the identification $D = \mu'(C)$, a phenomenological definition of diffusion coefficient.

This derivation (in particular, the assumption that $\mu = \mu(C)$) assumes that concentration gradients are negligible. If a glassy solid changes from a vitreous to a crystalline condition (i.e., if devitrification occurs), then concentration gradients may not be negligible. (Cahn [10] substantiates this for borosilicate glass.) In this case, the chemical potential μ will depend on both C and gradients of C. In Appendix A we shall show that this dependence is given by

$$\mu = f'(C) - k\nabla^2 C, \tag{2.6}$$

where $f(C)$ is a certain energy density. Now, the mass current $\underline{J}$ driven by the gradient of μ is given by

$$\underline{J} = - \text{grad}\, \mu = - \text{grad}\, f'(C) + k\, \text{grad}\, \nabla^2 C\ . \tag{2.7}$$

In this case, the basic continuity equation becomes

$$\frac{\partial C}{\partial t} = -\operatorname{div} \underline{J} = \operatorname{div} \operatorname{grad} \mu \tag{2.8}$$

$$= \nabla^2 (f'(C) - k\nabla^2 C)$$

$$= -k\nabla^4 C + \operatorname{div}(f''(C) \operatorname{grad} C) .$$

Finally, if we incorporate chemical dynamics (or reaction terms) or concentration dependent dissolution rates as in [2] and [4], we obtain

$$\frac{\partial C}{\partial t} = -k\nabla^4 C + \operatorname{div}(f''(C) \operatorname{grad} C) + G(C). \tag{2.9}$$

In the one-dimensional case, which we study in the next section, equation (2.9) becomes

$$\frac{\partial C}{\partial t} = -k \frac{\partial^4 C}{\partial x^4} + \frac{\partial}{\partial x}\left(f''(C)\frac{\partial C}{\partial x}\right) + G(C) . \tag{2.10}$$

Equation (2.10) is highly nonlinear, and thus, solving specific problems could be a formidable task (although much could probably be learned about the structure of various solutions by sophisticated perturbation and bifurcation procedures). Certainly, in the early stages of any leaching problem it is valid to consider the appropriate linearized equation. Depending upon the time scales of interest and the relative sizes of various parameters and concentration amplitudes, this early stage may mean large numbers of years, but, of course, such an estimate would need to be substantiated either by corroborating experiments, an assessment of the neglected nonlinear terms, or appropriate asymptotic methods on the full nonlinear problem.

Clearly, equation (2.10) implies that any linearized problem to be considered in the early leaching stages involves an equation of the form

$$\frac{\partial C}{\partial t} = -\alpha \frac{\partial^4 C}{\partial x^4} + \beta \frac{\partial^2 C}{\partial x^2} + h(C_s - C) \tag{2.11}$$

where α, β, h, and C_s are constants. In the next section we examine an appropriate problem involving (2.11) to find what leaching time law is implied.

3. The time law for leaching:

We study the transport model of Godbee and Joy [2] replacing their mechanism of Fickian diffusion with the generalized diffusive mechanism developed in Section 2. Thus, we consider the following linearized problem of diffusion from a semi-infinite solid waste:

$$\frac{\partial C}{\partial t} = -\alpha \frac{\partial^4 C}{\partial x^4} + \beta \frac{\partial^2 C}{\partial x^2} + h(C_s - C), \tag{3.1}$$

$$C(o,t) = 0, \tag{3.2}$$

$$\frac{\partial^2 C(o,t)}{\partial x^2} = 0, \tag{3.3}$$

$$C(x,o) - C_s \ . \tag{3.4}$$

Here C is the concentration of the mobile form of some diffusing species. The initial concentration C_s of this species is assumed at saturation level for this species in the waste solid, and the rate at which less mobile forms are converted to more mobile forms is proportional to the difference $(C_s - C)$ between the saturation value C_s and instantaneous concentration C. Thus, h is a dissolution rate constant. α and β are constants determined from the phenomenological constants and linearization of ((2.10). The justification and derivation of the boundary condition (3.3) is given in appendix B.

Let $u(x,t) = C_s - C(x,t)$. Then, $u(x,t)$ satisfies

$$\frac{\partial u}{\partial t} = -\alpha \frac{\partial^4 u}{\partial x^4} + \beta \frac{\partial^2 u}{\partial x^2} - h u \ , \tag{3.5}$$

$$u(o,t) = C_s \ , \tag{3.6}$$

$$\frac{\partial^2 u(o,t)}{\partial x^2} = 0 \ , \tag{3.7}$$

(3.8) $$u(x,o) = 0 \ .$$

The problem (3.5)-(3.8) can be solved efficiently by employing a Fourier sine transform in x. Thus, define

(3.9) $$\tilde{u}(k,t) = \int_0^\infty u(x,t) \sin kx \, dx, \quad u(x,t) = \frac{2}{\pi} \int_0^\infty \tilde{u}(k,t) \sin kx \, dk.$$

Then, apply this transform in the usual way to obtain

(3.10) $$\frac{d\tilde{u}}{dt} + (\alpha k^4 + \beta k^2 + h)\tilde{u} = (\alpha k^3 + \beta k)C_s \ ,$$

(3.11) $$\tilde{u}(k,o) = 0 \ ,$$

the solution of which is

(3.12) $$\tilde{u}(k,t) = \frac{(\alpha k^3 + \beta k)C_s}{\alpha k^4 + \beta k^2 + h} \left[1 - e^{-(\alpha k^4 + \beta k^2 + h)t} \right] .$$

Therefore,

(3.13) $$u(x,t) = \frac{2C_s}{\pi} \int_0^\infty \frac{(\alpha k^3 + \beta k)\left[1 - e^{-(\alpha k^4 + \beta k^2 + h)t} \right]}{\alpha k^4 + \beta k^2 + h} \sin kx \, dk \ .$$

It is interesting to note that the integral representation (3.13) has several non-uniformities. For example,

$$\lim_{x \to \infty} \int_0^\infty \neq \int_0^\infty \lim_{x \to \infty} \ .$$

Nevertheless, we can assess the large x behavior by an appropriate asymptotic analysis as follows: First, write (3.13) as

$$(3.14)\qquad u(x,t) = \frac{2C_s}{\pi}\int_0^\infty \frac{(\alpha k^4+\beta k^2+h-h)}{\alpha k^4+\beta k^2+h}\,\frac{\sin kx}{k}\,dk$$

$$-\frac{2C_s}{\pi}\int_0^\infty \frac{(\alpha k^4+\beta k^2+h-h)\,e^{-(\alpha k^4+\beta k^2+h)t}}{\alpha k^4+\beta k^2+h}\,\frac{\sin kx}{k}\,dk$$

$$=\frac{2C_s}{\pi}\int_0^\infty \frac{\sin kx}{k}\,dk - \frac{2C_s h}{\pi}\int_0^\infty \frac{\sin kx}{k(\alpha k^4+\beta k^4+h)}\,dk$$

$$-\frac{2C_s}{\pi}\int_0^\infty \frac{e^{-(\alpha k^4+\beta k^2+h)t}}{k}\sin kx\,dk$$

$$+\frac{2C_s h}{\pi}\int_0^\infty \frac{e^{-(\alpha k^4+\beta k^2+h)t}}{k(\alpha k^4+\beta k^2+h)}\sin kx\,dk\,.$$

Now, in the integrals let $kx = s$ and use the fact that $\int_0^\infty \frac{\sin s}{s}\,ds = \frac{\pi}{2}$ to obtain that as $x \to \infty$,

$$(3.15)\quad u(x,t) = C_s - \frac{2C_s h}{\pi}\int_0^\infty \frac{1}{\alpha\frac{s^4}{x^4}+\beta\frac{s^2}{x^2}+h}\,\frac{\sin s}{s}\,ds$$

$$-\frac{2C_s}{\pi}\int_0^\infty e^{-\left(\alpha\frac{s^4}{x^4}+\beta\frac{s^2}{x^2}+h\right)t}\,\frac{\sin s}{s}\,ds$$

$$+\frac{2C_s h}{\pi}\int_0^\infty \frac{e^{-\left(\alpha\frac{s^4}{x^4}+\beta\frac{s^2}{x^2}+h\right)t}}{\alpha\frac{s^4}{x^4}+\beta\frac{s^2}{x^2}+h}\,\frac{\sin s}{s}\,ds$$

$$\sim C_s - \frac{2C_s}{\pi}\int_0^\infty \frac{\sin s}{s}\,ds - \frac{2C_s e^{-ht}}{\pi}\int_0^\infty \frac{\sin s}{s}\,ds + \frac{2C_s e^{-ht}}{\pi}\int_0^\infty \frac{\sin s}{s}\,ds$$

$$= 0.$$

Therefore, $u(x,t) \to 0$ as $x \to \infty$ for fixed t which is, of course, consistent with our originally posed boundary value problem (3.5)-(3.8).

To determine the amount of material leached in the early stages we shall first carry out an asymptotic expansion of the solution (3.13) for small t and then for small x. Let $kx = s$ in (3.13), so that (3.13) becomes

$$(3.16)\qquad u(x,t) = \frac{2C_s}{\pi x}\int_0^\infty \frac{\alpha\frac{s^3}{x^3}+\beta\frac{s}{x}}{\alpha\frac{s^4}{x^4}+\beta\frac{s^2}{x^2}+h}\sin s\,ds$$

$$-\frac{2C_s}{\pi x}\int_0^\infty \frac{\left(\alpha\frac{s^3}{x^3}+\beta\frac{s}{x}\right)e^{-\left(\alpha\frac{s^4}{x^4}+\beta\frac{s^2}{x^2}+h\right)t}}{\alpha\frac{s^4}{x^4}+\beta\frac{s^2}{x^2}+h}\sin s\,ds$$

$$=\frac{2C_s}{\pi x}\int_0^\infty \frac{\alpha\frac{s^3}{\eta^3}t^{1/4}+\beta\frac{s}{\eta}t^{3/4}}{\alpha\frac{s^4}{\eta^4}+\beta\frac{s^2}{\eta^2}t^{1/2}+ht}\sin s\,ds$$

$$- \frac{2C_s e^{-ht}}{\pi x} \int_0^\infty e^{\frac{-\alpha s^4}{\eta^4}} \left[\frac{\left(\frac{\alpha s^3}{\eta^3} t^{\frac{1}{4}} + \frac{\beta s}{\eta} t^{\frac{3}{4}} \right) e^{\frac{-\beta s^2}{\eta^2} t^{\frac{1}{2}}}}{\frac{\alpha s^4}{\eta^4} + \frac{\beta s^2}{\eta^2} t^{\frac{1}{2}} + ht} \right] \sin s \, ds,$$

where $\eta = \frac{x}{t^{\frac{1}{4}}}$. Thus, for <u>fixed</u> η, we have that asymptotically as $t \to 0$,

$$(3.17) \quad u(x,t) \sim \frac{2C_s}{\pi x} \int_0^\infty \frac{\eta}{s} t^{\frac{1}{4}} \sin s \, ds - \frac{2C_s e^{-ht}}{\pi x} \int_0^\infty e^{\frac{-\alpha s^4}{\eta^4}} \left[\frac{\eta}{s} t^{\frac{1}{4}} + O(t^{\frac{3}{4}}) \right] \sin s \, ds$$

$$\sim C_s - \frac{2C_s(1-ht)}{\pi x} \int_0^\infty e^{\frac{-\alpha s^4}{\eta^4}} \frac{\eta}{s} t^{\frac{1}{4}} \sin s \, ds$$

$$\sim C_s - \frac{2C_s}{\pi} \int_0^\infty e^{\frac{-\alpha s^4}{\eta^4}} \frac{\sin s}{s} \, ds$$

The last integral in (3.17) can not be evaluated in closed form, but clearly it is some function of η. Denote it by $g_0(\eta)$. Therefore,

$$u(x,t) \sim C_s - g_0(\eta) \quad \text{as} \quad t \to 0, \quad \text{where} \quad \eta = \frac{x}{t^{\frac{1}{4}}}.$$

Clearly, from (3.17) the general functional form of the small time asymptotic expansion is

$$(3.18) \quad u(x,t) \sim C_s - g_0(\eta) - g_1(\eta) t^{\frac{1}{2}} + \ldots \quad \text{as} \quad t \to 0, \quad \text{where} \quad \eta = \frac{x}{t^{\frac{1}{4}}},$$

and $g_0(\eta)$ and $g_1(\eta)$ are certain integrals defining functions of fixed η.

Before we discuss (3.18) let us examine (3.13) asymptotically for small x. Again we start by letting $kx = s$ in the integrand, so that (3.13) becomes

$$(3.19)\qquad u(x,t) = \frac{2C_s}{\pi x}\int_0^\infty \frac{\alpha\frac{s^3}{x^3} + \beta\frac{s}{x}}{\alpha\frac{s^4}{x^4} + \beta\frac{s^2}{x^2} + h}\sin s\, ds$$

$$- \frac{2C_s}{\pi x}\int_0^\infty \frac{\left(\alpha\frac{s^3}{x^3} + \beta\frac{s}{x}\right)e^{-\left(\alpha\frac{s^4}{x^4} + \beta\frac{s^2}{x^2} + h\right)t}}{\alpha\frac{s^4}{x^4} + \beta\frac{s^2}{x^2} + h}\sin s\, ds$$

$$\sim \frac{2C_s}{\pi}\int_0^\infty \frac{\sin s}{s}\, ds - \frac{2C_s}{\pi}e^{-ht}\int_0^\infty e^{-\alpha\frac{s^4}{x^4}t}\,\frac{\sin s}{s}\, ds$$

$$\sim C_s - \frac{2C_s}{\pi}e^{-ht}\int_0^\infty e^{\frac{-\alpha t}{x^4}s^4}\left[1 - \frac{s^2}{6} + \ldots\right] ds$$

$$\sim C_s - \frac{2C_s}{\pi}(1-ht)\left[\frac{\Gamma(\frac{1}{4})}{4\alpha^{\frac{1}{4}}}\frac{x}{t^{\frac{1}{4}}} - \frac{\Gamma(\frac{3}{4})}{24\alpha^{\frac{3}{4}}}\left(\frac{x}{t^{\frac{1}{4}}}\right)^3 + \ldots\right]$$

Therefore,

$$(3.20)\qquad u(x,t) \sim C_s - \frac{2C_s}{\pi}\left[\frac{\Gamma(\frac{1}{4})}{4\alpha^{\frac{1}{4}}}\frac{x}{t^{\frac{1}{4}}} + \frac{\Gamma(\frac{3}{4})}{24\alpha^{\frac{3}{4}}}\left(\frac{x}{t^{\frac{1}{4}}}\right)^3\right] \text{ as } x \to 0, \text{ fixed } t.$$

The asymptotic estimates (3.18) and (3.20) clearly show that in the early stages of leaching $u(x,t)$ depends on the simularity variable $\eta = x/t^{\frac{1}{4}}$. Thus, at any concentration level we have a diffusion front with position proportional to $t^{\frac{1}{4}}$ rather than the standard $t^{\frac{1}{2}}$ found in problems involving the standard second order diffusion equation. To assess the time

dependence of the quantity Q leached from the solidified waste we must calculate the total amount of diffusing species which has left the medium at time t. To do this we first calculate the flux $\underline{J}$ across the surface at $x = 0$. Now, from (2.4) and (2.6), or as we show in greater detail in Appendix A,

$$(3.21) \qquad \underline{J}\Big|_{x=0} = \alpha \frac{\partial^3 C(o,t)}{\partial x^3} - \beta \frac{\partial C(o,t)}{\partial x}$$

Upon using the asymptotic expansion (3.20), we see immediately that

$$(3.22) \qquad \underline{J}\Big|_{x=0} \sim (\text{constant}) t^{-3/4} + (\text{constant}) t^{-1/4} ,$$

so that the total amount Q is given by

$$(3.23) \qquad Q = \int_0^t \underline{J}\Big|_{x=0} dt \sim (\text{constant}) t^{1/4} + (\text{constant}) t^{3/4} .$$

Therefore, the time law for the early stages of leaching implied by the generalized diffusion model is of the form

$$(3.24) \qquad Q = At^{1/4} + Bt^{3/4} .$$

The constants A and B can be determined empirically in any given application, and also, clearly, by more detailed asymptotics on this or more realistic geometries they can be determined phenomenologically in terms of the fundamental parameters of the diffusion model. By normalizing both (1.1) and (3.24) to a common value at some instant we see immediately that (3.24) predicts both larger initial quantities and faster initial leach rates than (1.1) thus providing a possible mechanism to account for the observed larger leached quantities and leach rates for various devitrified glassy materials and other waste solids.

4. Accounting for radioactive decay

So far we have not considered radioactive decay. We have assumed that the isotope being removed from the waste product is a stable one. To account for radioactive decay we can proceed as follows: If the radioactive isotope under consideration has a simple one-step decay to a stable form, then a simple standard exponential factor with the relevant half-life constant can easily be incorported into our calculations. This is done in [2]. However, many isotopes (the actinides, for example) have complex decay chains with daughters first displaying a growth with time followed eventually with decay. In these cases an effective decay factor between two given times can be deduced from experimental data and then applied to the appropriate time law (1.1) or (3.24). This approach is used in [4]. In any event the appropriate formulas for Q is of paramount importance.

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APPENDIX A

Appendix A. Generalized Diffusion Equations

Rather than derive the standard classical diffusion equation by postulating Fick's law as done in most presentations, it is possible to derive the equation and Fick's law itself from a basic energy argument. It is this appeal to the fundamentals of the physics which allows and even suggests the necessary generalizations.

Perhaps the best way to present the derivation is first to discuss the Classical Fick's law in the relevant notation. Thus, suppose $C(\underline{x},t)$ represents the concentration of some diffusing species. Let $f(C)$ represent the free energy density (i.e., internal energy per unit volume) of the system, so that the total energy $F[C]$ in a volume V is

$$F[C] = \int_V f(C)\, d\underline{x}. \tag{A.1}$$

The variational derivative $\frac{\delta F}{\delta C}$ (that is, the change in energy or work done in changing states by an amount δC) defines a (chemical) potential $\mu(C)$; that is,

$$\mu(C) = \frac{\delta F}{\delta C} = f'(C) \tag{A.2}$$

Now, a gradient of the potential μ will drive a current $\underline{J}$, or equivalently, flux $\underline{J}$ is proportional to the gradient of μ. This is Fick's law, Thus,

$$\underline{J} = -D \text{ grad } \mu(C), \tag{A.3}$$

where D is a proportionality constant. The basic equation of continuity (i.e., conservation of mass) then becomes

$$\frac{\partial C}{\partial t} = -\text{ div } \underline{J} = \text{div } (D \text{ grad } \mu(C)) = \text{div } (Df''(C) \text{ grad } C) \tag{A.4}$$

Hence,

$$\frac{\partial C}{\partial t} = \text{div}\,(\tilde{D}(C)\ \text{grad}\ C), \tag{A.5}$$

where

$$\tilde{D}(C) = D f''(C) \tag{A.6}$$

In the case of the simple heat equation or a situation with constant diffusion, the internal energy density is the standard quadratic form $f(C) = \frac{1}{2}C^2$. Then, $\mu(C) = C$, and (A.5) becomes

$$\frac{\partial C}{\partial t} = D\,\nabla^2 C \tag{A.7}$$

with $\tilde{D}(C) \equiv D$ representing the constant diffusion coefficient. Classical Fickian nonlinear diffusion is represented by (A.5) with a nonlinear diffusivity $\tilde{D}(C)$. Clearly, the derivation remains the same if we allow D to have spatial and temporal dependence, if we allow C to be a vector of concentrations, and if we add sources and sinks (i.e., dynamics or reaction terms) to the continuity equation to obtain the standard reaction-diffusion system

$$\frac{\partial C}{\partial t} = \text{div}(\tilde{D}(\underline{C},\underline{x},t)\text{grad}\ C) + G(\underline{C}) \tag{A.8}$$

in place of (A.5). Here $\underline{G}(\underline{C})$ represents the dynamics (or reaction terms) or concentration dependent dissolution rates. This completes our derivation of Fickian diffusion.

Most derivations of (A.5) or (A.8) start at equation (A.3); that is, Fick's law as given in (A.3) is simply postulated. All we have done is to start with the internal energy (consistent with Fick's law) necessary to maintain states described by Fick's law. The pertinent feature of this energy functional (A.1) is that it depends only on the state C of the system through

the density $f(C)$. This assumes that diffusion distances and concentration amplitudes are such that concentration gradients are negligible. If a glassy solid changes from a vitreous to a crystalline condition (i.e., if devitrification occurs), then concentration gradients may not be negligible, and a gradient energy may be necessary to describe the system. That is, phenomenologically, instead of (A.1) a more realistic energy functional is

$$F[C] = \int_V \left[f(C) + \tfrac{1}{2}k(\nabla C)^2 + k_1\nabla^2 C + \ldots\right]d\underline{x} \,. \tag{A.9}$$

The form of the energy density is consistent with the requirements that the energy density must be invariant under reflections $(x_i \to -x_i)$ and rotations $(x_i \to x_j)$. Here $f(C)$ represents the energy density which this volume would have in a composition in which gradients are negligible, and the other terms represent the energy density (a "gradient" energy) which is contributed by the now non-neglibible concentration gradients. This is the crucial step in assessing the physical role of diffusion. Our derivation most closely follows the work of Cahn [10]-[12] and Landau-Ginzburg (see [15], [16]).

Now, we simply re-trace the steps in going from (A.1) to (A.8). The potential μ induced by our energy functional (A.9) is given by

$$\mu = \mu(C,\nabla C) = \frac{\delta F}{\delta C} = - k\nabla^2 C + f'(C), \tag{A.10}$$

so that the flux $\underline{J}$ is given by

$$\underline{J} = - D \text{ grad } \mu(C,\nabla C). \tag{A.11}$$

The equation of continuity then becomes

$$\frac{\partial C}{\partial t} = - \text{ div } \underline{J} = \text{div } (D \text{ grad } \mu) \tag{A.12}$$

$$= D\,\nabla^2(-\,k\nabla^2 C + f'(C))$$

$$= -\,kD\,\nabla^4 C + \operatorname{div}\,(D\,f''(C)\,\operatorname{grad} C)\ .$$

The basic Landau-Ginzburg assumption for $f(C)$ is that

$$f(C) = \tfrac{1}{2}AC^2 + \tfrac{1}{4}BC^4 \qquad \text{(A.13)}$$

Only even powers of C appear because the energy density can not depend on the sign of C. Thus, (A.12) becomes

$$\frac{\partial C}{\partial t} = -\,Dk\nabla^4 C + DA\,\nabla^2 C + DB\,\nabla^2 C^3\ . \qquad \text{(A.14)}$$

Finally, if we incorporate the dynamics (or reaction terms), we obtain

$$\frac{\partial C}{\partial t} = -\,Dk\nabla^4 C + DA\,\nabla^2 C + DB\,\nabla^2 C^3 + G(C)\ . \qquad \text{(A.15)}$$

The equations (A.14), (A.15) are the generalizations of equations (A.5), (A.8) respectively. In the one-dimensional case equation (A.15) becomes

$$\frac{\partial n}{\partial t} = -\,Dk\,\frac{\partial^4 n}{\partial x^4} + D(A+3Bn^2)\,\frac{\partial^2 n}{\partial x^2} + 6DBn\left(\frac{\partial n}{\partial x}\right)^2 + G(n)\ . \qquad \text{(A.16)}$$

In the context of the thermodynamics of phase transition the constant A in (A.13) is given by

$$A = A_o(T - T_C)\ , \qquad \text{(A.17)}$$

where A_o is some constant, T is the temperature, and T_C is the critical temperature. Thus, the parameter A can assume positive or negative values. Therefore, if we designate the coefficient DA of the second derivative in

(A.14) as the "diffusion coefficient," then negative diffusion is possible. The stabilizing mechanism then becomes the fourth order term. In applications to problems involving metal alloys where the effects of elasticity may be important Cahn [11] has added elastic strain energy terms to the basic energy functional (A.9). In these applications for problems with both positive and negative values of A the theory has been successful both qualitatively and quantitatively.

APPENDIX B

Appendix B. Boundary conditions for the generalized diffusion equation

The boundary conditions appropriate for a given problem can be determined from the variational principle governing the problem [17]-[19]. For the spatial boundary conditions given by (3.2) and (3.3) it is sufficient to consider the equilibrium (or steady state) equation, namely

$$(B.1) \qquad -\alpha \frac{\partial^4 C}{\partial x^4} + \beta \frac{\partial^2 C}{\partial x^2} + h(C_s - C) = 0.$$

This is the Euler equation which comes from the Lagrangian $L(C, C_x, C_{xx})$ given by

$$(B.2) \qquad L(C, C_x, C_{xx}) = \frac{1}{2}\alpha C_{xx}^2 + \frac{1}{2}\beta C_x^2 + \frac{1}{2}h(C_s - C)^2 .$$

That is equation (B.1) is the Euler equation which results from the variational calculation

$$(B.3) \qquad \delta \int_0^\infty L(C, C_x, C_{xx})dx = 0.$$

For arbitrary variations δC equation (B.3) becomes

$$(B.4) \qquad \int_0^\infty \left(L_C - \frac{d}{dx} L_{C_x} - \frac{d^2}{dx^2} L_{C_{xx}}\right)\delta C \, dx + \left[L_{C_x} - \frac{d}{dx} L_{C_{xx}}\right]\delta C\Big|_0^\infty + L_{C_{xx}} \delta C_x\Big|_0^\infty = 0$$

Now, from the usual fundamental lemma of the calculus of variations we must have

$$(B.5) \qquad L_C - \frac{d}{dx} L_{C_x} - \frac{d^2}{dx^2} L_{C_{xx}} = 0,$$

which is precisely the steady state equation (B.1). For the problem we discuss in Section 3 we are requiring that the concentration $C(x,t)$ vanishes at the surface $x = 0$ and as $x \to \infty$. Thus, our admissible class of variations

must require that $\delta C = 0$ at $x = 0$ and as $x \to \infty$. Therefore, (B.4) implies that

$$L_{C_{xx}} \delta C_x \Big|_0^\infty = 0 \tag{B.6}$$

In the calculus of variations (B.6) is known as a natural boundary condition. Since δC_x is arbitrary within the class of admissible variations, we must take $L_{C_{xx}} = 0$ at $x = 0$ and as $x \to \infty$ to have a well-posed boundary value problem. Therefore, $C_{xx} = 0$ at $x = 0$, so that

$$\frac{\partial^2 C(o,t)}{\partial x^2} = 0 \tag{B.7}$$

is the necessary second boundary condition.